



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

RECEIVED
EPA 0010

2006 MAR -2 AM 9:28

201-14208

FEB 23 2006

Mr. G.L. McCallister
Director, Regulatory Affairs
Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Dear Mr. McCallister:

Thank you for your letter dated January 16, 2006, to Diane Sheridan, U. S. Environmental Protection Agency (EPA), regarding EPA's High Production Volume (HPV) Challenge Program.

In your letter, you answer four questions regarding the processing of acid chlorides, tallow, hydrogenated (CASRN 68955-37-3) that were posed by EPA in a May 24, 2005, letter to your company – Hercules Incorporated (Hercules). EPA asked these questions to aid us in making a final determination concerning your request in a January 18, 2005, letter to withdraw Hercules' sponsorship of CASRN 68955-37-3 under the HPV Challenge Program. Hercules asked to withdraw sponsorship of this chemical based on the contention that this substance should not be subject to the Program since it had been incorrectly classified as an isolated intermediate and mistakenly reported to the Inventory Update Rule (IUR). Based on all of the information Hercules has provided, the Agency is now able to make a determination regarding the classification of this chemical under the Toxic Substance Control Act (TSCA) and address your company's responsibility for CASRN 68955-37-3 under the HPV Challenge Program.

Based on the process description for CASRN 68955-37-3 provided by Hercules, EPA has concluded that this chemical is more appropriately classified as a non-isolated intermediate under TSCA (40 CFR §710.23) per your company's manufacturing process. Therefore, this chemical as processed by your company, as with all substances meeting the definition of a non-isolated intermediate under TSCA, is not reportable to the IUR pursuant to 40 CFR §§710.30(c) and 730.50(c). In line with this determination, the Agency recommends that Hercules amend its past IUR reporting records for this chemical.

In regards to Hercules' request to withdraw its sponsorship of CASRN 68955-37-3 under the HPV Challenge Program, any substance that is determined to be a "no longer HPV" chemical is no longer subject to the HPV Challenge Program. EPA posted draft guidance on procedures for removing "no longer HPV" chemicals from the scope of the HPV Challenge Program on its Chemical Right-to-Know (ChemRTK) website (www.epa.gov/chemrtk) in March 1999. According to this guidance, a chemical that has not been reported in HPV volume in the last two

Inventory Update Rule (IUR) reporting years (i.e., 1998 and 2002) and is not likely to become HPV again is no longer considered an HPV chemical for purposes of the Program. Based on our review, EPA has determined that CASRN 68955-37-3 **does not meet** the "no longer HPV" criteria because it has been reported to the Inventory in the last two IUR reporting periods by your company. However, should Hercules amend its IUR records as directed above to indicate that it no longer reports this chemical, EPA will be able reevaluate the "no longer HPV" designation for CASRN 68955-37-3 and release Hercules from any responsibility for the substance under the HPV Challenge Program.

We will post your letter, accompanied by our reply, on the ChemRTK website as soon as possible. Should you have any questions pertaining to this response, please contact Diane Sheridan at (202) 564-8176. If you have general questions concerning the HPV Challenge Program, please submit them through the ChemRTK website comment button or through the TSCA Assistance Information Service (TSCA Hotline) at (202) 554-1404. The TSCA Hotline can also be reached via email at tsc-hotline@epa.gov.

Sincerely,


Jim Willis, Director
Chemical Control Division

cc: AR-201



RECEIVED
OPPT CDIC

2006 JAN 27 AM 8:43

201-16184

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599
(302) 995-3000
www.herc.com

January 16, 2006

Ms. Diane Sheridan
U.S. Environmental Protection Agency
EPA-East
Mail Code 7405M
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

Dear Ms. Sheridan,

This letter is in response to a letter which I received some months ago from Mr. Jim Willis regarding our request to withdraw acid chlorides, tallow, hydrogenated, CASRN 68955-37-3 from the original HPV list. We have been in communication with EPA on this issue since 2Q04 and I apologize for the long delays in response.

Mr. Willis' letter to me is enclosed as Attachment A. I will answer each of his questions below in the order given on his letter.

1. The fatty acid chloride (FAC) is transferred from the reaction vessel via a vacuum siphon pump. It is an electro-mechanically driven process that permits separate of the top organic layer from the bottom aqueous layer in the reactor. There is no manual interaction or human exposure during this step. All materials remain in contiguous equipment.
2. The manufacturing and transfer processes all occur within enclosed contiguous equipment. The reactor vessels are connected via piping lines and the transfer is driven via pumps that are activated from a control room. There are no human exposures during this step.
3. Regarding hydrogenation: Hercules does not do the hydrogenation. The hydrogenated fatty acid is purchased as a raw material.
4. Regarding earlier 19989 and 2002 IUR reports: we questioned in 1998 (and before) whether the FAC was an isolated intermediate as defined under TSCA. At that time, the manufacturing process involved a longer holding time, presumably to effect better aqueous organic layer separation. It was thought that this might be considered as holding or storing the intermediate material. Being unclear, a conservative judgement was made to report the material as an isolated intermediate. The process has been improved since that time, as well as our understanding of the process such that we no longer feel this is an isolated intermediate from a TSCA perspective. The FAC is indeed an intermediate, but it is an in-process intermediate that is neither isolated nor removed from contiguous equipment in that process. It is transferred from the first reactor through a continuous process cleaner into a temporary hold tank until the full FAC batch has been cleaned. The cleaned FAC is then pumped into the second reactor where the final product, an alkyl ketene dimer, is manufactured. The residency time for the FAC in the temporary hold tank is <3 hours. The entire mfg process is less that one 8-hr shift. Based on the process changes and better understanding of the process timing, we have judged that this FAC under the current process is not an isolated intermediate by TSCA definition.

Ms. Diane Sheridan
U.S. Environmental Protection Agency

- 2 -

January 16, 2006

I trust this has sufficiently answered your questions. Please contact me if you need any additional information.

Sincerely,

G. L. McCallister
Director, Regulatory Affairs
Phone: (302) 995-3406
Fax: (302) 995-3445 FAX

GLM:clj
Attachment

2006letters.doc/2-3



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAY 24 2005

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Mr. G. L. McCallister
Director, Regulatory Affairs
Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, Delaware 19808-1599

Dear Mr. McCallister:

Thank you for your letter of January 18, 2005 to Karen Hoffman at the U.S. Environmental Protection Agency (EPA) regarding EPA's High Production Volume (HPV) Challenge Program.

Your letter advises EPA that Hercules is withdrawing sponsorship of acid chlorides, tallow, hydrogenated (CAS No. 68955-37-3) based on the fact that it was incorrectly identified as an isolated intermediate. Further, your letter states that this misidentification is sufficient to delete the chemical from the HPV Challenge Program, and cites that testing of this material would be moot and unnecessary given the health or environmental fate of this type of chemical. EPA has reviewed the supporting documentation that Hercules provided. Before a final determination can be made, additional information/clarification on the manufacturing process is needed as follows:

1. In Attachment 3, a detailed explanation on how the Fatty Acid Chloride (FAC) intermediate is transferred to the "holding tank." Is this a mechanical, gravitational or manual process?
2. Are the manufacturing and transfer processes enclosed at all times with respect to the FAC intermediate?
3. The intermediate is identified as a hydrogenated substance, but the hydrogenation process is omitted in the discussion in Attachment 3. At which point is the hydrogenation performed?
4. Why did the company report for this substance under the Inventory Update Rule (IUR) in 1998 and 2002? Was any amount of this substance ever sold or was it all consumed on site?

Please submit the additional information requested to Diane Sheridan, U.S. Environmental Protection Agency, EPA East - Mail Code 7405M, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460, or (sheridan.diane@epa.gov) . The Agency will review the requested information and respond accordingly.

We will post your letter, accompanied by our reply, on the ChemRTK website as soon as possible. Should you have any questions pertaining to this response, please contact Diane Sheridan at (202) 564-8176. If you have general questions concerning the HPV Challenge Program, please submit them through the ChemRTK website (www.epa.gov/chemrtk) comment button or through the TSCA Assistance Information Service (TSCA Hotline) at (202) 554-1404. The TSCA Hotline can also be reached via email at tsc hotline@epa.gov.

Sincerely,

Jim ~~Willis~~, Director
Chemical Control Division

cc: AR-201

HERCULES INCORPORATED
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JUN 07 2005
REGULATORY AFFAIRS
AND TOXICOLOGY



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

201-15918

MAY 24 2005

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Mr. G. L. McCallister
Director, Regulatory Affairs
Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, Delaware 19808-1599

Dear Mr. McCallister:

Thank you for your letter of January 18, 2005 to Karen Hoffman at the U.S. Environmental Protection Agency (EPA) regarding EPA's High Production Volume (HPV) Challenge Program.

Your letter advises EPA that Hercules is withdrawing sponsorship of acid chlorides, tallow, hydrogenated (CAS No. 68955-37-3) based on the fact that it was incorrectly identified as an isolated intermediate. Further, your letter states that this misidentification is sufficient to delete the chemical from the HPV Challenge Program, and cites that testing of this material would be moot and unnecessary given the health or environmental fate of this type of chemical. EPA has reviewed the supporting documentation that Hercules provided. Before a final determination can be made, additional information/clarification on the manufacturing process is needed as follows:

1. In Attachment 3, a detailed explanation on how the Fatty Acid Chloride (FAC) intermediate is transferred to the "holding tank." Is this a mechanical, gravitational or manual process?
2. Are the manufacturing and transfer processes enclosed at all times with respect to the FAC intermediate?
3. The intermediate is identified as a hydrogenated substance, but the hydrogenation process is omitted in the discussion in Attachment 3. At which point is the hydrogenation performed?
4. Why did the company report for this substance under the Inventory Update Rule (IUR) in 1998 and 2002? Was any amount of this substance ever sold or was it all consumed on site?

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2005 MAY 26 AM 11:39

Please submit the additional information requested to Diane Sheridan, U.S. Environmental Protection Agency, EPA East - Mail Code 7405M, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460, or (sheridan.diane@epa.gov) . The Agency will review the requested information and respond accordingly.

We will post your letter, accompanied by our reply, on the ChemRTK website as soon as possible. Should you have any questions pertaining to this response, please contact Diane Sheridan at (202) 564-8176. If you have general questions concerning the HPV Challenge Program, please submit them through the ChemRTK website (www.epa.gov/chemrtk) comment button or through the TSCA Assistance Information Service (TSCA Hotline) at (202) 554-1404. The TSCA Hotline can also be reached via email at tsc-hotline@epa.gov.

Sincerely,

Jim Wilks, Director
Chemical Control Division

cc: AR-201

201-15852

HERCULES

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19806-1589
(302) 995-3000
www.herc.com

January 18, 2005

Ms. Karen S. Hoffman
U.S. Environmental Protection Agency
7405M USEPA Headquarters, Ariel Rios Building
1200 Pennsylvania Avenue, N. W.
Washington, DC 20460

RECEIVED
DPPT CBIC
05 APR -4 PM 1:31

Dear Karen:

This is a follow up to several communications that we have had regarding Hercules' HPV Challenge commitment to CASRN: 68955-37-3; acid chlorides, tallow, hydrogenated. Hercules had sent a memo to Mr. Charlie Auer on 21-Apr-04 (see Attachment 1, your doc #201-15258) regarding status of this HPV chemical. In response, you sent an e-mail date 23-June-04 (see Attachment 2) indicating that the information Hercules sent to Mr. Auer was not relevant to CASRN 68955-37-3. relevant to this HPV substance. You are correct and I apologize for the confusion. Please disregard our 21-Apr-04 letter to Mr. Auer as it is not relevant to CASRN 68955-37-3, but rather to the end product produced from that intermediate.

After further research into the guidelines and intent of the HPV program, as well as review of our own manufacturing process for CASRN 68955-37-3, Hercules respectfully wishes to withdraw its commitment to test this material. Our reasoning is based on two arguments:

1. Hercules feels that it was incorrectly identified as an isolated intermediate. You will find in Attachment 3, a brief description of the manufacturing process we use to make this intermediate. While it is indeed, a chemical intermediate, it is not stored, isolated or removed from the manufacturing equipment. As such, there is little or no potential for health or environmental exposure.
2. While Hercules feels that reason #1 is sufficient to delete this chemical from the HPV program, we also provide additional information which we hope will help convince EPA that testing of this material would be moot and unnecessary given the health or environmental fate of this type of chemical. We offer this additional information as Attachment 4.

Thank you in advance for your review and consideration in this matter. Please feel free to contact me if you have any questions or comments on this information we have presented.

Sincerely,

G. L. McCallister
Director, Regulatory Affairs

GLM:cj
Attachments

FAC1_HPVIetter.doc/1-2

Attachment 1

201-15258

HERCULES

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599
(302) 995-3000
www.herc.com

April 21, 2004

Administrator
U.S. Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116

Attn: Chemical Right-to-Know Program

RE: Attached letter from Mr. Charles Auer regarding unsponsored chemical

Dear Administrator,

Enclosed is a copy of a recent letter we received from Mr. Charles Auer regarding our participation in the HPV Program. In that letter, Mr. Auer indicates that we have not submitted a test plan for a chemical to which we had originally committed. The chemical is identified in the attachment to that letter.

Please be advised that shortly after we had sent out commitment to EPA in the Fall of 1999, we formed a consortium with several international partners and agreed to sponsor this chemical under the ICCA HPV Program. Also enclosed is a copy of the letter that was sent to Mr. Auer in the Fall of 1999 describing that commitment, the consortium members and the chemicals they were sponsoring.

That program is well advanced at this point in time. SIDS dossier is in preparation. I trust this satisfies your immediate concerns. Should you need additional information, please do not hesitate to contact me.

Sincerely,

G. L. McCallister
Director, Regulatory Affairs

GLM:cj
Enclosures

2004letters.doc/9

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MAY 11 PM 12:40



**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460**

APR 12 2004

**OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES**

**Mr. G.L. McCallister
Hercules Incorporated
1313 North Market Street
Wilmington, DE 19894-0001**

Dear Mr. McCallister:

I want to personally acknowledge and thank you for your commitment to the High Production Volume (HPV) Challenge Program. Participation in the HPV Challenge Program has exceeded EPA's expectations and, although the success of the program has been significant, there are a number of commitments that have not yet been met and are considered late. Preparations are underway for release of the HPV Challenge Program Status Report in May, 2004. The HPV Challenge Program Status Report will identify those sponsors whose commitments are overdue.

Our records indicate that your organization has sponsored the chemical(s) listed in the attached table for a start year of 2003 or earlier but robust summary and test plan information has not been received by the Agency. The commitment start year indicates the year of the Program in which sponsors agreed to begin the evaluation of each chemical by submitting robust summaries of existing data and a test plan showing how the sponsor plans to fill any data gaps. Under the HPV Challenge Program, all test plans and robust summary submissions should be submitted in the year indicated. Any needed new testing on the HPV chemicals in the HPV Challenge Program is to be completed by the end of 2004 with all data to be made available to the public by 2005. So that the Agency may meet its HPV Challenge Program's objectives, we are no longer accepting changes to start years and commitments not yet fulfilled are considered late.

While we are not accepting changes to start years, the Agency does expect sponsors to uphold their commitments and submit test plans and robust summaries as soon as possible. If no test plan/robust summary submission is received before the end of 2004 for these commitments, then the Agency will consider these chemicals as "orphans"—or unsponsored. Chemicals not voluntarily sponsored in the HPV Challenge Program will become candidates for test rules under Section 4 of the Toxic Substances Control Act (TSCA).

The Agency understands that over time, for a variety of reasons, sponsorship plans may change; however, it is incumbent upon sponsors of unmet commitments to update the Agency so that its records may accurately reflect the current commitment status. Information should be sent to:

Administrator
US Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116
Attention: Chemical Right-to-Know Program

or through e-mail at: oppt.ncic@epa.gov and chem.rtk@epa.gov by April 30, 2004. Please note that any correspondence containing Confidential Business Information (CBI) should not be sent to the above address or through e-mail.

If you have any questions or concerns, please contact Karen Lannon of my staff at 202-564-8163. Thank you.

Sincerely,

Charles M. Auer
Director
Office of Pollution Prevention and Toxics

Attachment

HERCULES INCORPORATED
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APR 19 2004

REGULATORY AFFAIRS
AND TOXICOLOGY

Hercules Incorporated — Overdue Commitments

CAS Number	9 th Collective Index Name	Start Year
68955-37-3	Acid chlorides, tallow, hydrogenated	2002

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel : +49-69-2558-1341
Fax : +49-69-2558-1342
e-mail: Ungeheuer@VCI.de

Verband Tegewa
Karlsruhe 21
D-60329 Frankfurt

Mr Charles M. Auer
Director, Chemical Control Division
U.S. Environmental Protection Agency
401 M Str., S.W. (7405 Rm E 403)
Washington, DC 20460
USA

November 30 1999
Unge0007

ICCA-Commitment / US HPV Challenge Program

Dear Mr Auer

Please find enclosed for your information the commitment of the task force "Global Producers of AKD" to sponsor Alkylketendimer (AKD) in the frame of the ICCA-HPV-Initiative.

The task force represents the following companies:

- EKA Chemicals AB
 - Hercules BV
 - Kemira Chemicals Oy
 - Ralsio Chemicals Oy
- BASF Aktiengesellschaft
- NOF Corporation

Would you be so kind to send us an acknowledgement that AKD is no longer directly a subject of the US-challenge program.

Yours sincerely

Global Producers of AKD

Enclosure

Dr. Peter Ungeheuer

GLOBAL PRODUCERS OF AKD

Dr Peter Ungshauer
Tel: +49-69-2556-1341
Fax: +49-69-2556-1342
e-mail: Ungshauer@VCI.de

Verband Tagawa
Karlstraße 21
D-60329 Frankfurt

Fax +32-2-676-7332

Mr Shiva Bhushana Rao
Chemical Resources Unit Manager
European Chemical Industry Council
(CEFIC)

November 30 1999
Ungsh004

ICCA Commitment for Alkylketendimer (AKD)

Dear Mr Bhushana Rao

On behalf of the producers of AKD in the US, Europe and Japan, namely the companies

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Raisio Chemicals Oy

we would like to inform you that the above mentioned companies have formed a consortium called

"Global producers of AKD"

to commit themselves to the ICCA HPVC program for AKD.

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel : +49-69-2558-1341
Fax : +49-69-2558-1342
e-mail: Ungeheuer@VCI.de

Verband Tagawa
Karlstraße 21
D-60329 Frankfurt

Fax: +1-703-741-6098

Mr Frederick C. McElowney
Product Stewardship Team
Chemical Manufacturers Association
(CMA)

November 30 1999
Ungh/004

ICCA Commitment for Alkylketendimer (AKD)

Dear Mr McElowney

On behalf of the producers of AKD in the US, Europe and Japan, namely the companies

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Ralsio Chemicals Oy

we would like to inform you that the above mentioned companies have formed a consortium called

"Global producers of AKD"

to commit themselves to the ICCA HPVC program for AKD.

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel: +49-69-2556-1341
Fax: +49-69-2556-1342
e-mail: Ungeheuer@VCI.de

Verband Tagewe
Karlstraße 21
D-60329 Frankfurt

Fax: +81-3-3580-0764

Mr Masatoshi Ogura
General Manager
Task Force Team for ICCA
JCIA

November 30 1999
Ungh/004

ICCA Commitment for Alkylthetandimer (AKD)

Dear Mr Ogura

On behalf of the producers of AKD in the US, Europe and Japan, namely the companies

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Ralato Chemicals Oy

we would like to inform you that the above mentioned companies have formed a consortium called

"Global producers of AKD"

to commit themselves to the ICCA HPVC program for AKD.

The commitment covers the following individual substances which will be handled as a family

10126-68-8	4-heptadecylidene-3-hexadecyloxetan-2-one
42272-70-8	4-pentadecylidene-3-tetradecyloxetan-2-one
55680-03-0	4-undecylidene-3-decyloxetan-2-one
58000-16-9	(Z,Z)-4-(heptadec-8-enylidene)-3-(hexadec-7-enyl)oxetan-2-one
67845-94-7	4-heptadecylidene-3-tetradecyloxetan-2-one
67845-95-8	3-hexadecyl-4-pentadecylidenecyclohexan-2-one
68390-58-7	Fatty acids, tallow, hydrogenated, dimers, diketene derivatives
68558-25-2	1,9-Octadecadien-1-one, (Z)-, dimer
84989-41-3	2-Oxetanone, 3-C12-16-alkyl-4-C13-17-alkylidene deriva.
94109-14-5	2-heptadecylidene-4-hexadecyloxetan-3-one
98248-87-8	2-Oxetanone, 3-C14-16-alkyl-4-C15-17-alkylidene deriva.

The necessary testing will start in the year 2000.

The undersigned will act as contact point.

Kind regards

Global Producers of AKD

Dr Peter Ungeheuer

Vice-Director Association TEGEWA e.V.

Attachment 2



Hoffman.Karen@epa
mail.epa.gov

06/23/2004 02:00 PM

To: gmccalister1@herc.com
cc: cjenkins@herc.com, rhartgrove@herc.com
Subject: Question concerning your letter to EPA Administrator re: CAS
68955-37-3

Dear Mr. McCallister:

We received your letter of April 21, 2004. (see attached pdf file below) in response to a letter from Charles Auer concerning Hercules' sponsorship of CAS 68955-37-3. In your letter, you attached a previous letter sent in the fall of 1999 giving a list of your chemicals that were now going to be sponsored under the Global Producers of AKD through the ICCA program.

However, CAS 68955-37-3 is not included in this list.

In order that we can correct our records, please respond to this question as soon as you can via email to me and clarify whether Hercules intended for CAS 68955-37-3 to be included with the list of chemicals that were to have gone to the Global Producers of AKD.

Thank you for your prompt attention to this matter.

Sincerely,

Karen Hoffman

----- Forwarded by Karen Hoffman/DC/USEPA/US on 06/23/04 12:41 PM -----

NCIC HPV
Sent by: Michael
Leczyński/DC/USEPA/US@EPA, Vanessa
Ofner
Larona
Karen
Boswell/DC/USEPA/US@EPA,
05/11/04 01:53 PM
Sheridan/DC/USEPA/US@EPA, Peter
Deena Vann/DC/USEPA/US@EPA,
Taylor/DC/USEPA/US@EPA, Karen
Kearney/DC/USEPA/US@EPA,

To: Barbara
Williams/DC/USEPA/US@EPA,
Washington/DC/USEPA/US@EPA,
Hoffman/DC/USEPA/US@EPA, Karen
Diane
Wendolkowski/DC/USEPA/US@EPA,
Jeffrey
Lannon/DC/USEPA/US@EPA, Renee
Jim Alwood/DC/USEPA/US@EPA
cc:
Subject: Hercules (201-15258)

- Commitment Scanned Files

This e-mail contains the following commitment letter, which was received from Hercules Incorporated.

1. The .gif format of the following item is attached:

201-15258 - c15258a.gif
 c15258b.gif
 c15258c.gif
 c15258d.gif
 c15258e.gif
 c15258f.gif
 c15258g.gif
 c15258h.gif
 c15258i.gif

2. The .pdf format of the following item is attached:

201-15258 = 201-15258.pdf

There are 10 files attached.

(See attached file: c15258a.gif) (See attached file: c15258b.gif) (See attached file: c15258c.gif) (See attached file: c15258d.gif) (See attached file: c15258e.gif) (See attached file: c15258f.gif) (See attached file: c15258g.gif) (See attached file: c15258h.gif) (See attached file: c15258i.gif) (See attached file: 201-15258.pdf)

Please contact me if there are any questions or comments regarding these attachments. Thank you.

Michael Ofner
Contractor for EPA

         
c15258a.gif c15258b.gif c15258c.gif c15258d.gif c15258e.gif c15258f.gif c15258g.gif c15258h.gif c15258i.gif 201-15258.pdf

Attachment 3: General Information Regarding the Manufacturing Process

Hercules manufactures tallow fatty acid chlorides via halogenation of tallow fatty acid using phosphorus trichloride. The fatty acid chloride (FAC) intermediate is pumped into four tanks to separate by-products. Excess phosphorus trichloride is removed, organic and aqueous layers are separated, and the FAC intermediate is transferred to a process holding tank. The intermediate resides here, on average, only an hour or so. It is important to note that this not a storage tank as such but rather a "wide spot" in the manufacturing process prior to manufacture of the ketene dimer AKD via a semi-continuous process.

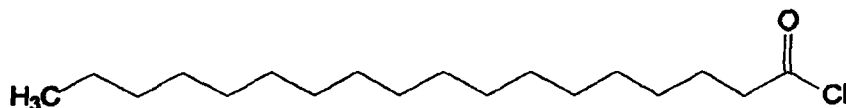
The FAC intermediate is semi-continuously removed from the holding tank into a reactor to make the final dimer product. The FAC is contained within contiguous tanks and transfer lines throughout the process. There are no steps that physically isolate or remove the intermediate from the process.

An estimated 40,000 pounds of dimer product may be produced during a single shift; thus the contents of the "holding" tank are quickly turned over. Hercules does not move the FAC intermediate from site to site. All FAC manufactured at a given site is consumer at that site.

Hercules considers this substance as a non-isolated intermediate with essentially no exposure. Thus, we feel it is not subject to the HPV program.

Attachment 4: Chemical and Environmental Fate of Fatty Acid Chlorides

The fatty acid (FA) from which CASRN: 68955-37-3; acid chlorides, tallow, hydrogenated, is generated is typically a mixture of C16 and C18 saturated (stearic and palmitic acids). Below is a diagram of a typical FA chloride, stearyl chloride in this case: CASRN 112-76-5.



Research indicated that FA chlorides will hydrolyze readily in the presence of moisture to hydrochloric acid and the corresponding fatty acid (see attachment 5: Bauer. S.T., and Curet. M.C., *Journal of the American Oil Chemists' Society*, Feb., 1947, The Hydrolysis of Fatty Acid Chlorides). This research indicated that stearyl chloride and pamityl chloride hydrolyzed almost completely within 4-5 hours.

Hercules argues that this hydrolysis will occur regardless of whether the FA chloride was introduced into the environment (such as waterways) or into a biological system (such as ingestion by an animal). Thus, the health and environmental effects of this fatty acid chlorides (and probably most other fatty acid chlorides) are determined by the health and environmental fate of the hydrolysis product. The health and environmental effects of hydrochloric acid are reasonably well known and predictable. The fatty acid hydrolysis products, stearic and palmitic in this case, are common fatty acids with many industrial and food uses, and are themselves, listed as HPV chemicals.

Thus, Hercules argues that the health and environmental effects of this specific HPV substance, CASRN 68955-37-3, will have already been established by virtue of known effects from hydrochloric HPV summaries prepared for stearic and palmitic acids.

acids are not available. Thus, as a result of their shortage of fats and oils during the war, the Germans used a linseed oil soap in the manufacture of Buna. This actually served a real function yet it did greatly slow down their production. Later when even this became unavailable they used synthetic fatty acid prepared by the oxidation of Fischer Tropch paraffin.

Research work in this country has shown that synthetic rubber can be made from polyunsaturated acids and other low grade fatty acids at present production rates if special activators are used to compensate for the inhibiting effects. However, these types of rubber have never been tested extensively on a commercial scale and do introduce a number of new difficulties into the manufacturing operations.

Trends in the Manufacture of Soaps for Use in Making Synthetic Rubber

There has been a noticeable trend in the fatty acids or soaps used in the manufacture of synthetic rubber. At first distilled myristic and palmitic acid from spermaceti was used. This was replaced soon by distilled myristic acid from coconut fatty acids. When the supply of this became short, soap made from selectively hydrogenated tallows and greases was used. Large scale manufacture of GR-S necessitated larger quantities of soap. This was obtained first from high grade edible tallow and finally from hydrogenated oils, tallows, and greases.

Future developments point to the use of highly purified fatty acids or soaps having a definite ratio

of the various fatty acids present. Crystallized acids are quite satisfactory and uniform in their activity. For example, crystalline palmitic acid would be desirable in certain cases while for others a crystallized high purity oleic acid free from polyunsaturated would be ideal. Improvement in crystallization processes and development of markets for the polyunsaturated acids obtained as by-products will help to bring these things to pass. Proper economic analysis of the technological progress in the related fields will certainly determine the course of the future in this field.

The author wishes to acknowledge the assistance obtained from the unpublished summaries and specifications contributed by the scientists and companies who have participated in the synthetic rubber program.

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The Hydrolysis of Fatty Acid Chlorides

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IN the course of the preparation of a series of synthetic glycerides of known molecular configuration it was necessary to store the acid chloride (1) intermediates for various periods of time. The freshly distilled acid chlorides were stored in sealed glass ampoules and analyzed prior to use. After several months of storage under these conditions no appreciable hydrolysis could be detected. It was realized, however, that under commercial conditions of storage more or less hydrolysis might occur from the presence of moisture, and it appeared advisable, therefore, to determine the relative rates of decomposition of the more commonly used saturated and unsaturated fatty acid chlorides.

A search of the literature revealed little information on the relative rates of hydrolysis of acid halides. Velasco and co-workers (4, 6) investigated the velocities of hydrolysis of acetyl chloride, chloroacetyl chloride, propionyl chloride, and butyryl chloride. The degree of hydrolysis was determined by measuring the extent of diffusion of the reaction products into water and toluene at 25° C. and 45° C. These investigators reported that hydrogen ions do not catalyze any of the hydrolytic reactions of the chlorides, which would indicate that the mechanism of hydroly-

sis in this case is different from that of the esters and amides of the fatty acids. Similar results have been reported by Velasco and Ollero (5) and by Karvė and Dolé (2, 3) with respect to the rates of hydrolysis of a number of aromatic acid chlorides. The acid halides used by the latter investigators were dissolved in chloroform or benzene and shaken with water at constant rate. Hydrolysis was found to occur at the boundary between the two liquid phases at rates which were determined by diffusion of the reactant and reaction products across the interfacial boundary. The rate constants were found to increase with increasing concentration of acid halide. The hydrochloric acid formed during hydrolysis was found to exert no catalytic action. Conical flasks were said to favor the hydrolysis.

Since there are no available data on the hydrolysis of the higher fatty acid chlorides, experiments were made to determine the hydrolysis of a number of saturated and unsaturated fatty acid chlorides when shaken with water for varying periods of time.

Experimental

Purification of the Fatty Acids and Preparation of Fatty Acid Chlorides. The saturated and unsaturated fatty acids, with the exception of octanoic and decanoic, were purified by the method described by Bauer (1). Commercial preparations of octanoic and

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TABLE 1
Hydrolysis of Saturated Fatty Acid Chlorides

Time Minutes	Fatty acid chloride					
	Octanoyl	Decanoyl	Lauryl	Myristyl	Palmityl	Stearyl
	Mole % unhydro- lyzed	Mole % unhydro- lyzed	Mole % unhydro- lyzed	Mole % unhydro- lyzed	Mole % unhydro- lyzed	Mole % unhydro- lyzed
5	99.0	94.7	96.8	98.4	95.6	99.0
15	79.8	89.4	95.2	95.4	89.9	14.0
30	68.4	82.3	94.0	90.8	82.8	7.7
60	48.0	73.8	90.1	84.1	57.3	2.2
120	34.6	59.9	79.0	74.0	35.3	1.3
180	25.1	50.7	72.2	55.8	3.3	0.1
240	22.3	45.6	65.2	45.8	1.7	1.3
300	22.3	45.3	55.7	37.2	3.0	0.9
360	22.7	44.2	51.4	33.5	2.7	1.3
420	22.7	44.7	48.4	25.2	2.5	1.6
480	27.7	49.7	40.4	19.0	3.8
540	27.4	4.4
600	27.1	4.3
1440	16.9	5.4
1800	18.09	5.4
2100	18.99
2400	14.30

decanoic acids were fractionally distilled, and that fraction selected whose neutralization equivalent corresponded most nearly to the theoretical value.

The acid chlorides were prepared by reaction of the fatty acids with a suitable chlorinating agent according to previously described methods (1). The acid chloride was distilled and sealed in glass ampoules until used. The purity of each preparation was determined by weighing a one-gram sample of the acid chloride into a 50-ml. glass-stoppered Erlenmeyer flask to which was added 20 ml. of a 20% aniline-ether solution. After the reaction was completed, 2 ml. of concentrated hydrochloric acid was added to convert the excess aniline to the hydrochloride. The ether was removed by evaporation on the steam bath and the aniline hydrochloride and mineral acid were removed by washing the anilide repeatedly with distilled water. The free fatty acid content of the anilide solution was determined by dissolving the residue in 25 ml. of hot neutral alcohol and titrating the solution with 0.1 N sodium hydroxide. Analysis of the acid chlorides used in this work indicated a purity of 99.2% or better on the assumption that free fatty acid was the only impurity present.

Hydrolysis of the Fatty Acid Chlorides. A portion (approximately 0.9-1.0 g.) of acid chloride was placed into a 50-ml. glass-stoppered Erlenmeyer flask which was placed on a mechanical agitator. A 10-ml. head was added to the flask and 5 ml. of distilled water was added from a pipette. The agitator was a modification of Camp's shaking apparatus imparted a planetary motion to the contents of the flask through a pulley-driven shaking platform.

The acid chloride-water mixture was shaken at room temperature (25° C.) for various intervals of time after which the reaction was stopped by the addition of 10 ml. of a 20% aniline-ether solution to convert the unhydrolyzed portion of acid chloride to the corresponding anilide.

The free fatty acid content of the anilide-fatty acid mixture was determined by titration with one-tenth normal sodium hydroxide solution. Since any free fatty acid which may have been present in the original chloride is titrated along with that produced by hydrolysis, the observed value of the latter must be corrected by subtraction of the previously determined value for the former.

TABLE 2
Hydrolysis of Unsaturated Fatty Acid Chlorides

Time Minutes	Fatty acid chloride		
	Elaidyl	Oleoyl	Linoleyl
	Mole % unhydro- lyzed	Mole % unhydro- lyzed	Mole % unhydro- lyzed
5	97.6	96.9	97.3
15	94.8	94.9	96.8
30	91.1	95.2	96.4
60	88.9	87.3	78.9
120	78.4	79.7	64.0
180	71.1	71.5	50.3
240	68.5	68.9	46.9
300	66.4	66.7	44.6
360	67.7	61.5	48.8
420	69.3	51.3	48.9
480	12.3	16.8
540	1.5
1440	1.5
1800	11.56
2100
2400	0.5

In order to compare the relative rates of hydrolysis of the acid chlorides it is necessary to express the results on a mole percentage basis. This may be done by means of the following equation:

Mole per cent of unhydrolyzed acid chloride equals

$$\frac{\text{moles original acid chloride} - (\text{moles NaOH} - \text{moles free fatty acid in original acid chloride})}{\text{moles original acid chloride}} \times 100$$

or

$$\frac{W_0 - W_1}{M. W. \text{ chloride}} - \left(\frac{\text{ml. NaOH} \times \text{normality}}{1000} - \frac{W_2}{M. W. \text{ acid}} \right) \times 100$$

$$\frac{W_0 - W_1}{M. W. \text{ chloride}}$$

where W_0 = weight of sample, and W_1 = weight of free fatty acid in the original sample of acid chloride used for hydrolysis.

TABLE 3
Specific Reaction Rate Constants for Hydrolysis of Fatty Acid Chlorides at 25° C.

Reaction time Minutes	Fatty acid chloride									
	Octanoyl	Decanoyl	Lauryl	Myristyl	Palmityl	Stearyl	Elaidyl	Oleoyl	Linoleyl	
	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	k × 10 ⁶	
5	14.52	6.71	7.54	3.23	9.00	22.31	4.86	2.21	5.88	
15	15.04	8.97	8.28	3.14	7.19	121.1	8.56	2.10	7.17	
30	15.19	4.98	2.96	3.23	6.39	85.5	2.11	1.64	6.45	
60	12.22	5.66	1.74	2.89	9.51	2.15	6.48	5.25	
120	9.35	4.41	1.39	2.31	11.25	2.09	5.44	
180	3.77	1.31	2.37	1.90	5.99	
240	1.75	2.35	1.96	
300	1.95	2.39	2.06	
360	1.85	2.12	2.04	
420	1.99	2.33	2.29	
480	1.99	2.46	
540	1.80	4.35	2.34	
600	1.90	2.90	4.51	
1440	1.94	2.93	

constants determined only to point of apparent equilibrium.

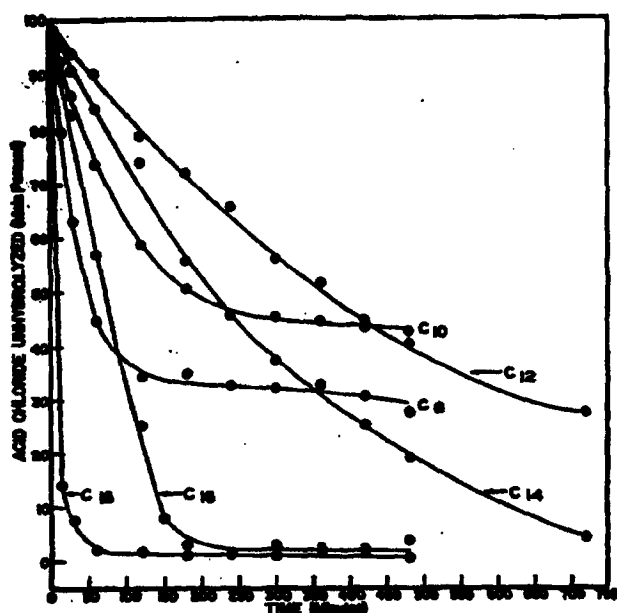


FIG. 1. Hydrolysis of saturated acid chlorides in water at 25° C.

Discussion of Results

Data relative to the hydrolysis of the chlorides of the even-numbered saturated fatty acids from caprylic to stearic are given in Tables 1 and 3 and graphically in Figures 1 and 3. It is evident from the curves in Figure 1 that of the chlorides investigated lauryl chloride is the most resistant and stearyl chloride the least resistant to hydrolysis. Stearyl chloride was essentially completely hydrolyzed after shaking with water for two hours at 25° C., whereas lauryl chloride was hydrolyzed to the extent of only 21% under the same conditions.

Experiments in which weighed amounts of acid chlorides were shaken with 0.1 N hydrochloric acid solution showed that the hydrogen ion had little if any effect on the rate of hydrolysis. Addition of small amounts of free fatty acids to the acid chloride prior to hydrolysis likewise appeared to have no effect on the rate of decomposition of the chloride.

Data with reference to the hydrolysis of the unsaturated fatty acid chlorides are given in Tables 2 and 3 and graphically in Figures 2 and 4. It is apparent from Figure 2 that elaidyl chloride is more resistant to hydrolysis than either oleyl or linoleyl chlorides. The linoleyl and oleyl chlorides hydrolyze at approximately the same rates during the first hour, but thereafter oleyl chloride hydrolyzes more rapidly than linoleyl chloride.

From calculations of specific reaction rates (Table 3) and plots of the logarithms of concentration of acid chloride vs. time, corresponding to various times of reaction (Figures 3 and 4), it appears that acid chlorides undergo hydrolysis in water to a point of apparent equilibrium. This equilibrium appears to take place after about 15 minutes of hydrolysis for stearyl chloride, 30 minutes for octanoyl chloride, 60 minutes for decanoyl and palmityl chlorides, 960 minutes (16 hours) for lauryl chloride, and 1,440 minutes (24 hours) for myristyl chloride. The unsaturated acid chlorides reach the point of equilibrium at 60 minutes for oleyl chloride, 180 minutes for linoleyl chloride, and 960 minutes for elaidyl chloride.

Several hypotheses may be advanced to explain the difference in the rates of hydrolysis between the C_8 , C_{10} , and the C_{12} to C_{18} saturated acid chlorides and the apparent equilibrium reached in the case of the shorter chain compounds. The decrease in the reaction rate of the fatty acid chlorides from C_8 to C_{12} may be attributed to decreasing activity of the acid chloride with increasing chain length. The increasing reaction rates of the fatty acid chlorides from C_{12} to C_{18} probably due to the increase in melting point and decrease in solubility of the fatty acids, liberated by hydrolysis, in the unhydrolyzed fatty acid chloride. This would result in a more complete withdrawal of the reaction products from the interface at which the reaction occurs. The fact that the hydrolysis of the shorter chain fatty acid chlorides reaches an apparent equilibrium before the acid chloride is completely hydrolyzed indicates the probable formation of a mono-molecular layer of free fatty acid at the interface which inhibits contact between the unhydrolyzed acid chloride and water. Further experimental data would be required to substantiate these hypotheses.

Summary

Fatty acid chlorides of octanoic, decanoic, lauric, myristic, palmitic, stearic, oleic, elaidic, and linoleic acids were hydrolyzed at 25° C. in water and the amounts of unchanged acid chlorides determined after different periods of reaction.

Contrary to expectations, the chlorides of the long chain fatty acids, palmitic and stearic, reacted at a more rapid rate than the chlorides of the shorter chain fatty acids. Lauryl chloride appears to be more resistant to hydrolysis than the shorter chain fatty acid chlorides.

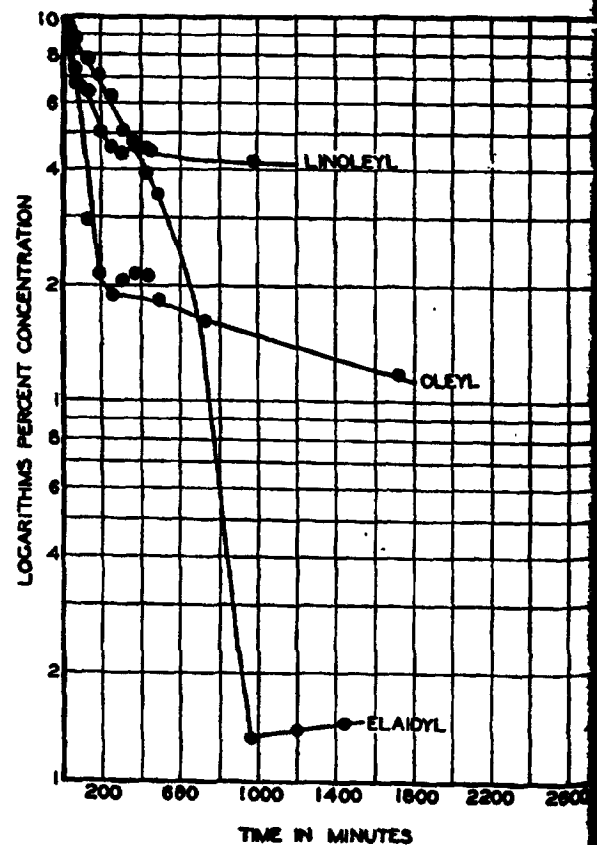


FIG. 2. Hydrolysis of unsaturated acid chlorides in water at 25° C.

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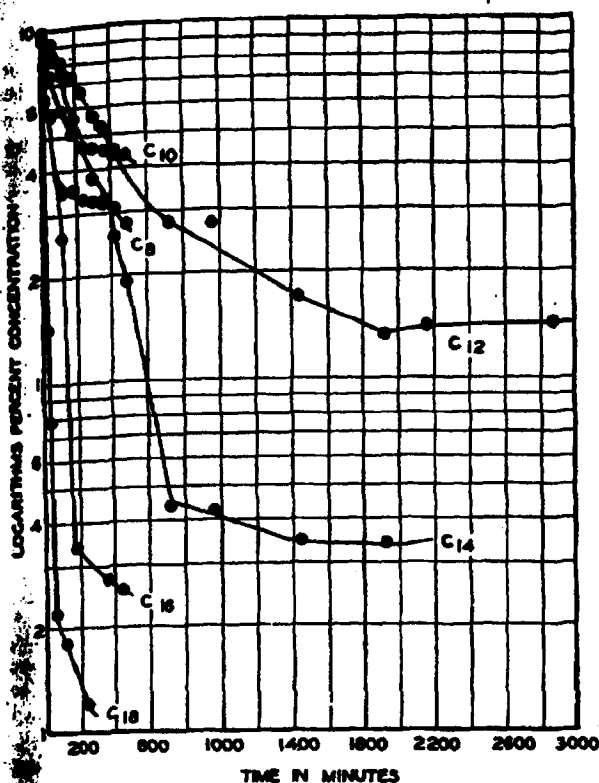


Fig. 3. Hydrolysis of saturated acid chlorides in water at 25° C.

ant to hydrolysis than either the chlorides of the lower molecular weight octanoic and decanoic acids or the chlorides of the higher molecular weight myristic to stearic acids.

The chlorides of the unsaturated acids, oleic, elaidic, and linoleic, are hydrolyzed less rapidly than stearyl chloride. However, elaidyl and myristyl chlorides exhibit the same relative rates of hydrolysis during the

first two hours of reaction. Myristyl chloride hydrolyzes more rapidly than elaidyl chloride after the first two hours.

The addition of either hydrochloric acid or free fatty acids to the reaction mixture was found to have no pronounced effect on the hydrolysis of the acid chlorides.

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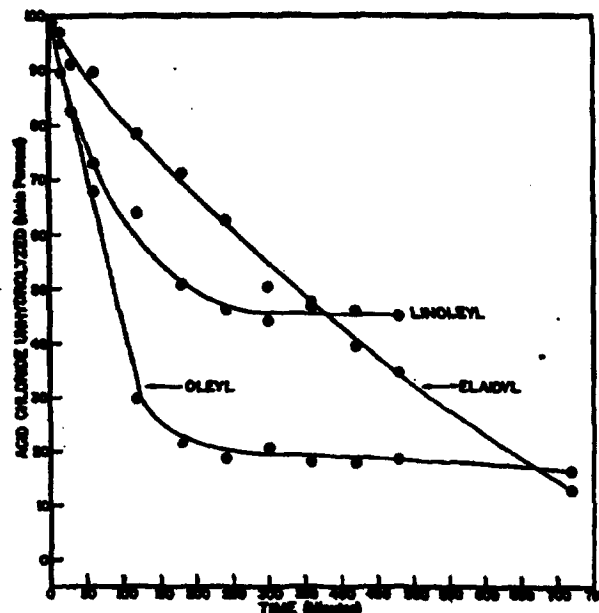


Fig. 4. Hydrolysis of unsaturated acid chlorides in water at 25° C.

A Study of Rancidity of Olive Oils

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INVESTIGATION of the problem of rancidity is rendered difficult by the fact that the ultimate standards to which all data must be referred are based on taste and smell. Among the aims of these experiments were: a) the comparison of the various known chemical tests for rancidity of fats and oils with the organoleptic test for the purpose of selecting the most reliable one for further use as a standard of reference; b) determination whether olive oils from different localities have different susceptibility to fat oxidation and the study of the effect of various factors and treatments upon such susceptibility to oxidation; and c) determinations whether anise seeds and cardamom seeds have antioxidant value for olive oil.

The methods used were the following:

1. The oxidizability-value developed by Imogio and modified by Kerr (1), which gives the amount of water-soluble oxidizable substances expressed in $O_2/100$ gm.

The Kreis (2) test which is based on the presence in rancid fats of epiphydrin aldehyde, an oxidation product of acrolein. It consists in the treatment of the oil with hydrochloric acid and a solution of phloroglucinol in ether.

Fellenberg (3) test based on the presence of aldehydes in the oxidized fats. Vintilescu and Popesco (4) test based on the presence of peroxides and oxides formed during the development of rancidity.

The Wheeler's (5) iodimetric method of determining the peroxides formed in rancid fats.

The last method was carried out as follows: five g. of olive oil were dissolved in 50 ml. of a mixture of glacial acetic acid and chloroform (3:2 by volume), after which one ml. of saturated potassium iodide solution was added. The mixture was stirred by giving a rotary motion to the flask. Exactly one minute after addition of the potassium iodide, 100 ml. of water were added and the liberated iodine titrated with 0.01 *N* sodium thiosulphate, using starch as